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INVESTIGATION AND SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS

FINAL REPORT

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FINAL REPORT

INVESTIGATION AND SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS

This report covers a research program which began July 1, 1960 and ended September 30, 1961. The Principal Investigator was Dr. A. F. Isbell, the Research Associate, Dr. Hans Fernekess, and the Research Assistant, Mr. J. P. Berry. Mr. Berry was a graduate student who had just started work on his Ph.D. degree. He was not able to start work on this project until September 1, 1960, but worked on it from that time until its termination date. Dr. Fernekess was a post doctoral student from Germany who was unable to come to this country and begin work on the project until December 15, 1960. When it was learned in the Spring of 1961 that the project would probably not be renewed, Dr. Fernekess located another similar position at Yale University, making it necessary for him to cease work on this project on June 30, 1961.

Because of our limited personnel, we chose two areas of investigation. One of these was the reaction between dialkyl alkylphosphonates and metallic sodium, a reaction the Principal Investigator had accidentally encountered approximately nine years ago while engaged in a chemical corporation research contract at the Monsanto Chemical Laboratory in Anniston, Alabama. The second area of research was the investigation of methods for the synthesis of fluoroalkylphosphonates. The following is a summary of the work carried out in these two areas.

Study of the Reaction of Dialkyl Alkylphosphonates and Metallic Sodium

As mentioned earlier, the Principal Investigator had discovered some years earlier that when diisopropyl methylphosphonate is heated to approximately 110° with a fine dispersion of molten sodium a vigorous and even violent reaction was found to take place. We decided to carry out this reaction under more controlled conditions in order to learn the nature of the changes which took place. To do this, molten sodium was dispersed in an inert hydrocarbon solvent such as toluene, xylene, eicosane or HB-40 (a partially hydrogenated mixture of o-, m-, and p-terphenyl, commercially available from the Monsanto Chemical Company) at 110°, followed by the slow addition of the phosphonate ester. Since the resulting reaction is quite exothermic, the desired temperature was maintained by the rate of addition of the ester.

In general, there appeared to be two principal products of this reaction. One of these products was normally a gas and the second product was a solid which separated from the solvent as a white granular mass or as a semi-solid material or in some instances it dissolved in the solvent to form a clear gel. Which of these behaviors resulted was usually dependent upon the nature of the

phosphonate ester and to a degree on the inert solvent. For instance, the lower molecular weight esters, such as dimethyl methylphosphonate and diethyl ethylphosphonate, normally produced the granular white solids. Higher molecular weight esters such as dibutyl butylphosphonate produced a viscous gel in toluene, indicating that the solid was in solution at least to some degree. Esters of intermediate molecular weight such as diisopropyl methylphosphonate produced semi-solid products.

The gaseous product of these reactions was identified, by the use of gas chromatography, as a saturated aliphatic hydrocarbon. Surprisingly enough this hydrocarbon seemed to be derived from the alkyl group of the ester portion of the phosphonate molecule. For instance, ethane was the product from diethyl ethylphosphonate, propane was produced from diisopropyl methylphosphonate and n-butane was identified as a product of the reaction from di-n-butyl n-propylphosphonate. Gas chromatography indicated that the volatile products were composed almost exclusively of the saturated hydrocarbons. However, a careful analysis of the product from diethyl ethylphosphonate indicated that a trace of diethyl ether was also present and perhaps three unidentified compounds were present in minute amounts. When the butane from a butyl ester was analyzed by gas chromatography, minute quantities of five or six additional products were indicated on the chromatogram. All these results would lead one to estimate that at least 90% of the volatile products of these reactions was the saturated aliphatic hydrocarbon, corresponding to the phosphonate ester group.

A great many attempts were made to determine accurately the stoichiometry of this reaction under investigation. All our results point clearly to one mole of the phosphonate ester requiring one gram atom of metallic sodium. However, when attempts were made to determine the number of moles of hydrocarbon produced per mole of phosphonate ester, we first encountered the problem of attempting to measure accurately the amount of hydrocarbon gas evolved from a solution in which the hydrocarbon would normally be expected to have a pronounced solubility. Accurate measurements of gas volume can be made only when the temperature of the gas is uniform and the temperature is controlled accurately. Without having specialized equipment, such measurements can be carried out best at approximately ambient temperatures. However, it is only at temperatures near the boiling point of a solvent that the solubility of a gas in the solvent approaches zero. Since we found it necessary to make measurements of gas volumes around 25°, we recognized that the hydrocarbon gases might have high solubilities in the solvent at this temperature. To minimize the error we attempted to avoid conditions which would enable the evolved gases to redissolve. It is recognized that our experimentally determined molar ratio of gaseous hydrocarbon produced per mole of phosphonate ester was perhaps low but at least they seemed to be reasonably reproducible. On the basis of more than ten different runs the maximum yield of gaseous hydrocarbon appeared to be approximately 0.5 mole per mole of phosphonate ester. There was some variation between 0.3 and 0.5 mole of hydrocarbon per mole of phosphonate ester. When hydrocarbon solvents such as xylene were utilized the yield of hydrocarbon never exceeded the maximum value mentioned. On the other hand, for reasons not at all understood, when a large

excess of the phosphonate ester was employed in the place of the inert hydrocarbon solvent, hydrocarbon gas production was well below 0.1 mole per mole of phosphonate ester and in some runs virtually no gas was generated.

Another interesting observation involved the production of transient colors in certain reactions. Pronounced color production seemed to be limited to those reactions in which HB-40 was employed as the solvent. In such instances colors ranging from red to blue to green developed briefly on the surface and in the near vicinity of the sodium particles. Such colors occasionally spread throughout the reaction mixture when an excess of phosphonate ester was present in the solution but disappeared rapidly as the excess ester was consumed.

If the volatile product is a saturated hydrocarbon derived from the alkyl ester group, one must find the source of the additional hydrogen atom necessary for this conversion. The reaction of phosphonate esters with sodium have some of the characteristics of free radical reactions. Since sodium metal might be assumed to be free radical, such a reaction type might not be unexpected. For these reasons it was originally believed that the necessary hydrogen atom was in some way being abstracted from the solvent. This appeared plausible, especially where the solvent was toluene or xylene. It seemed likely that a hydrogen radical from the methyl group of toluene might be abstracted, producing a benzyl free radical which would probably stablize itself by dimerization to 1,2-diphenylethane. Numerous attempts were made to confirm this hypothesis; all met with failure. The solvent recovered from one of these reactions was distilled carefully but the entire material had a boiling poirt and other physical properties that corresponded only to toluene. Samples of toluene recovered from various runs were analyzed by gas chromatography and in all instances the recovered solvent produced a chromatogram identical with the solvent originally employed for the reaction. Not even trace amounts of suspicious by-products were detected. Undoubtedly the production of only small quantities of volatile material from those reactions in which an excess of the phosphonate ester functioned as the reaction solvent is important to the solution of this problem but until now we have been unable to develop an intelligent explanation for such behaviors.

An equally important part of this investigation involved the identification of the solid reaction product. This also turned out to be a formidable problem. The higher molecular weight products tended to form viscous gels at the elevated temperatures and, incidently, such gels usually foamed badly. On cooling such gels to room temperature, they became unstirrible, semi-solid masses having a consistency resembling freshly precipitated silicic acid. The more granular solids appeared to react readily with constituents in the air, indicating that these solids had rather high degrees of reactivity. It was first believed, and is still suspected, that these solid products were largely the monosodium salt of the phosphonic ester. It this is true, one of the alkyl ester groups was replaced by a sodium atom. Since it was believed that such a monosodium salt would be difficult to purify and identify as such, these products were dissolved in water, in which they were highly soluble, and the resulting aqueous solution was passed as rapidly as possible through Dowex 50 resin in the hydrogen ion form. The eluate, from which all sodium ions had been removed, was then freezed-dried as quickly as possible. Such sodium-free products were

produced from a variety of reactions in which various phosphonate esters had functioned as starting materials. In all instances the residues from such freeze-drying operations were viscous liquids which showed no tendency to crystallize nor to distil. These properties are characteristic of the monoesters of phosphonic acids in general. Such products were prepared, starting with diethyl ethylphosphonate, dimethyl methylphosphonate, dibutyl benzylphosphonate and diethyl phenylphosphonate. Neutralization equivalents of such products were often approximately 85% of the expected values for the various monoesters. It was recognized that such results might have been caused by small amounts of impurities One of these products was carefully prepared from diethyl phenylphosphonate and submitted for elemental analysis. The determined percentage composition of this product was: C 47.63, 47.92; H 6.28, 6.09; P 18.12, 18.29. The calculated percentage values for the monoethyl ester of phenylphosphonic acid are: C 51.62; H 5.96; P 16.64. Thus, it is seen that the recovered product was low in carbon, slightly high in hydrogen and significantly high in phosphorus. Assuming the presence of one phosphorus atom per molecule, the compounds analyzed for the composition $C_{6.75}H_{10.4}PO_3$.

The various viscous, freeze-dried residues were also heated under reflux with concentrated hydrochloric acid for a number of hours and the resulting solutions were evaporated to dryness. The residues originating with the esters of ethylphosphonic acid and methylphosphonic acid could not be induced to crystallize, probably because of the presence of certain impurities and the low melting points and hygroscopic properties of these phosphonic acids. On the other hand, when this same procedure was carried out with the product from dibutyl benzylphosphonate, crystalline benzylphosphonic acid, m.p. 165-167°, was recovered. The mixed melting point with authentic benzylphosphonic acid was not depressed. A similar hydrolysis product, originating with diethyl phenylphosphonate was recovered as a viscous oil, from which has separated a few crystals while standing in a desiccator for a period of about one month. The fact that this product has been very slow to crystallize, even though phenylphosphonic acid melts at approximately 160°, indicates that if phenylphosphonic acid is present, there is also present a considerable quantity of other substances.

This situation was investigated by paper chromatographic procedures. It was hoped that by a technique such as this we would be able to separate the freeze-dried residue into its components and possibly have some chance of identifying each of these. Numerous solvent systems were investigated for the chromatographic separation of the freeze-dried residue. This residue may have been composed of more than one compound but the chromatographs did not indicate this. That this might be essentially true was indicated by the results from a run starting with diethyl ethylphosphonate which produced a freeze-dried residue that gave a neutralization equivalents within 3% of the calculated value. As indicated earlier, other freeze-dried products gave neutralization equivalents which were lower than the calculated value by as much as 15%.

Since we have been unsuccessful in determining the exact nature of this reaction by the techniques mentioned, it appeared desirable to investigate the types of phosphorus esters which were capable of taking part in this reaction with metallic sodium. In order to accomplish this we synthesized or acquired in

other ways samples of various kinds of phosphorus esters. These included esters of phosphoric acid, dialkylphosphinic acid, trialkyl esters of phosphorous acid, esters of simple alkyl- and arylphosphonic acids and phosphonic esters having other functional groups within the same molecule. A summary of the results obtained with these compounds is indicated in Table I. One may draw a number of conclusions from the results contained in Table I. It is seen that the reaction with metallic sodium fails to take place with the trialkyl esters of phosphorous acid, the trialkylesters of phosphoric acid, and the alkyl esters of dialkylphosphinic acids. All the phosphonic esters tried to date have reacted readily. These include esters containing α-methylene groups such as the esters of methyl-, ethyl- and benzyl-phosphonic acids. Those containing no α-methylene groups, such as triethyl α , α-dimethyl phosphonoacetate, triethyl phosphonoformate and diethyl phenyl-phosphonate reacted with ease and appeared to give the same type of reaction.

One further significant observation involved the failure of diethyl ethyl-phosphonate to react with metallic sodium when the toluene was replaced by di-n-butyl ether. The reason for this behavior is not known at the moment.

We hope to continue the study of this reaction as time will permit. There are a number of rather obvious experiments which should be performed and which may give valuable information about this reaction. For one thing, we should study the utility of solvents other than the hydrocarbons we have employed successfully to date and the one ether which appeared to inhibit completely the reaction. Triethyl phosphonoformate should be investigated again since the reaction reported in Table I gave a greater quantity of gas than was produced by any other starting material and the gaseous product was not identified. Other phosphonate esters which should give useful information are diphenyl esters of alkyl- and aryl-phosphonic acids, esters of dialkylaminoformylphosphonic acids and similar compounds.

Synthesis of Fluorinated Phosphonates

The object of this work was to attempt the development of one or more methods for the synthesis of a series of fluoroalkylphosphonic acids and derivatives. To our knowledge, the only compound of this type which has been reported is trifluoromethylphosphonic acid, which was produced in a small amount by Haszeldine, J. Chem. Soc., 1954, 3598, by means of a sequence which does not appear to be at all generally useful. Since trifluoromethylphosphonic acid had been reported, we first attempted to synthesize this compound by way of certain other routes. The first route we considered was the Michaelis reaction between trifluorochloromethane and the sodium derivative of dibutyl phosphonate. Because of the known inertness of trifluorochloromethane, it was not expected to take part in the Michaelis reaction. However, it was found that an exothermic reaction took place when trifluorochloromethane was passed into a solution of the sodium derivative of dibutyl phosphonate in a hydrocarbon solvent at 100°. The hydrocarbon solvents employed were HB-40 (Monsanto Chemical Company) or toluene. An ether solvent, the dimethyl ether of diethylene glycol (Diglyme) was also employed in this reaction. Apparently the results with all three solvents were identical. The reaction which took place at 100° caused the separation of a rather large quantity of insoluble, gummy solid which contained both sodium chloride and sodium fluoride

in varying amounts. When the halide was added to a solution of dibutyl sodiophosphonate, the exothermic stopped when approximately 0.5 mole of the halide had been added to 1.0 mole of the sodiophosphonate. In addition to the solid product, a small amount of volatile product, b.p. 80-115° (0.2 mm.), was recovered from each reaction. This volatile product amounted to approximately 10 g. from 0.2 mole of reactants. The combined product from five reactions was carefully redistilled in an attempt to recover one or more pure products. However, the boiling point steadily increased and there was no evidence of a significant amount of a single pure substance. It appears that this Michaelis reaction produces a variety of complex products from which it is virtually impossible to isolate any single substance in a high degree of purity.

It was hoped that the tendency of the fluorine atoms to react might be greatly reduced if one employed trifluoroiodomethane as the halide in the Michaelis reaction. Trifluoroiodomethane was produced in 47-70% yields by the reaction between silver trifluoroacetate and elemental iodine. In a further attempt to prevent reaction of the fluorine atoms, a toluene solution of dibutyl sodiophosphonate was added slowly to a solution of trifluoroiodomethane in toluene at room temperature. Some heat was evolved, solid separated from the reaction mixture but distillation of the product gave approximately the same results as had been obtained previously in the Michaelis reaction.

Although there appeared to be little hope to success, one Arbuzov reaction was carried out by passing tricluoroiodomethane into triethyl phosphite at a temperature of 115°. Again no single, pure product could be isolated from this reaction, although the boiling point and refractive index of some of the product indicated it to be the not unexpected diethyl ethylphosphonate.

We now turned our attention to attempts to exchange the chlorine for fluorine atoms in diethyl trichloromethylphosphonate. Attempts were made to prepare this chlorinated ester by the reaction between carbon tetrachloride, phosphorus trichloride and aluminum chloride, followed by the reaction between the prepared complex and ethanol. This is similar to a procedure described by Kinnear and Perrin, J. Chem. Soc., 1952, 3437. However, the more successful method for producing the chlorinated ester involved the Arbuzov reaction between carbon tetrachloride and triethyl phosphite, utilizing the procedure of Benglesdorf and Barron, J. Am. Chem. Soc., 77, 2869 (1955). By means of this reaction, diethyl trichloromethylphosphonate was produced in 71.6-78% yields.

Our first attempted exchanged reaction employed argentous fluoride as the source of fluorine. When this compound was heated on the steam bath with diethyl trichloromethylphosphonate, a vigorous, exothermic reaction resulted. Since toluene extracted nothing from the resulting solid product, the white solid was heated with 6M. HCl. After a brief heating period, a considerable quantity of white solid began collecting in the reflux condenser. The nature of this solid, produced by the HCl treatment, was not immediately evident and certain pecularities of its behavior and of its formation confused the situation. Although this product possessed most of the properties of silica, it also appeared to sublime when heated with acetonitrile and it seemed to form only when all three starting materials-diethyl trichloromethylphosphonate, argentous fluoride and hydrochloric acid were mixed and heated. This product was finally proved to be slightly impure silica.

The aqueous hydrochloric acid filtrate from one of the reactions mentioned in the previous paragraph was found to contain a small quantity of white solid which melted over the range of 70-80°. It was first suspected that this might be trifluoromethylphosphonic acid, which has been reported by Haszeldine to melt at 81°. However, to complicate matters, trichloromethylphosphonic acid is also reported to melt at 81°. Since we were able to recover only a small quantity of crude product and it showed little tendency to separate into pure fractions, we decided to investigate a second exchange reaction.

The next reagent chosen was potassium fluoride, which appeared to react readily with diethyl trichloromethylphosphonate when the two reagents were heated together on a steam bath. Distillation of the reaction product produced an 83% yield of chloroform and a salt-like product which was not investigated. A check on the potassium fluoride showed it to be the dihydrate form. This interesting reaction is probably worthy of further investigation but we passed it by with the hope of finding the desired exchange reaction.

The next step was the investigation of the action of anhydrous potassium fluoride on diethyl trichloromethylphosphonate. The reaction was carried out by heating four moles of the salt per mole of ester. A variety of reaction times and temperatures were investigated. Reaction times varied from a few hours to as much as a week and reaction temperatures varied from 100 to 150°. During the heating it was noted that some of the original potassium fluoride appeared to dissolve in the ester and after further heating a solid appeared to separate from solution. After reaction, the product was recovered by distillation b.p. 80° (32 mm.). The best yield of this material resulted from a reaction time of 60 hours on a steam bath. The products from a number of reactions were combined and carefully redistilled, producing a material having b.p. 88.5-89.5°(47 mm.), n_D^{27} 1.3710, d_4^{27} 1.1399. This compound readily caused constriction of the pupils of the eye and was at first believed to be diethyl trifluoromethylphosphonate. However, it gave the following analysis:

		Calcd. for $C_5H_{10}PO_3F_3$	Calcd. for $C_4H_{10}PO_3F$
C	30.78, 30.83	29.14	30.78
H	6.23, 6.24	4.89	6.46
F	12.15, 12.20	27.66	12.18
P	19.97, 19.81	15.03	19.85

It is obvious that the compound is not $C_5H_{10}PO_3F_3$ (diethyl trifluoromethylphosphonate) and is $C_4H_{10}PO_3F$, the formula for diethyl phosphonofluoridate. This is further confirmed by the molecular refraction:

M. R. for $C_4H_{10}PO_3F$ (from Lorenz-Lorentz equation) = 31.04
M. R. for $C_4H_{10}PO_3F$ (summation of atomic refractions) = 31.382
M. R. for $C_5H_{10}PO_3F_3$ (from Lorenz-Lorentz equation) = 40.99
M. R. for $C_5H_{10}PO_3F_3$ (summation of atomic refractions) = 36.150

For diethyl phosphorofluoridate McCombie and Saunders, Brit. Pat. 601, 210 (1948) gave b.p. 76-77° (25 mm.) and Menard and Jean, Bull. soc. chim. France, 1952, 544

gave n_D^{19} 1.3729 and $d_{17.3}$ 1.1512. We have more than 50 g. of diethyl phosphorofluoridate on hand and will be glad to send part or all to the U. S. Army Chemical Research and Development Laboratories, if requested.

Anhydrous sodium fluoride was employed in one reaction with diethyl trichloromethylphosphonate. Apparently, the same product was produced but the yield was only 29.7%, indicating that sodium fluoride is less effective in this reaction than potassium fluoride.

Before we learned that the product from diethyl trichloromethylphosphonate was diethyl phosphorofluoridate, we believed that we were producing the desired diethyl trifluoromethylphosphonate. Thus, it appeared desirable to investigate the reactions between anhydrous potassium fluoride and the diethyl esters of difluoromethylphosphonic and monofluoromethylphosphonic acids. The literature seems to record only one route to the esters of dichloromethylphosphonic acid. This involved the reaction between chloroform, phosphorus trichloride and aluminum trichloride by the method of Kinnear and Perren, J. Chem. Soc., 1952, 3437 to give dichloromethylphosphonyl dichloride, followed by the reaction of this acid chloride with ethanol to give the ethyl ester. Considerable difficulty was encountered in obtaining good yields of the acid chloride by the Kinnear and Perren reaction. This seemed to be caused by the slow hydrolysis of the aluminum chloride complex and the ease of hydrolysis of the acid chloride. This was solved, at least to some degree, by vigorous mixing of a methylene chloride solution of the complex with concentrated hydrochloric acid at about -20° followed by the rapid separation of the two phases and thorough drying of the methylene chloride solution before distillation. In this manner yields of up to 54.5% of the acid chloride resulted. The acid chloride was converted into the ethyl ester in a yield of 75%. When this diethyl dichloromethylphosphonate was heated with potassium fluoride there was essentially no evidence of reaction. Distillation of the product produced materials boiling over a rather wide range, indicating the production of small amounts of a variety of materials.

Diethyl monochloromethylphosphonate was produced by the reaction between ethanol and chloromethylphosphonyl dichloride (kindly supplied by the Monsanto Chemical Company). The yield of ester was 77.8%. This ester also failed to show any significant evidence of reaction when heated for prolonged periods of time at 100° with anahydrous potassium fluoride. In this instance it was possible to recover virtually all the starting materials. The recovered inorganic salt gave a negative test for chloride ion, indicating the complete absence of an exchange reaction.

We conclude that we have been unable so far to produce a fluoroalkylphosphonic acid or derivative by condensation of trifluorochloromethane or trifluoroiodomethane with dibutyl sodiophosphonate or triethyl phosphite. We have also been unable to bring about a fluorine-chlorine exchange reaction between esters of chloromethylphosphonic acids and argentous fluoride, potassium fluoride dihydrate, anhydrous potassium fluoride or sodium fluoride. The potassium fluoride dihydrate has been shown to cleave the carbon to phosphorous bond in diethyl trichloromethylphosphonate to produce chloroform in good yield as one of

the products. When anhydrous potassium fluoride is employed, again the carbon to phosphorus bond is cleaved to give in this instance diethyl phosphorofluoridate in excellent yield. Other products of these reactions have not been investigated and the nature of these unexpected reactions is not known.

Although our work to date has resulted in a complete failure to produce fluoroalkylphosphonate products, it has uncovered two interesting reactions. The first of these is the cleavage of diethyl trichloromethylphosphonate with potassium fluoride dihydrate to give chloroform as one of the products. The second cleavage product has not been investigated but we hope to do further work on this. The second reaction involves a cleavage of diethyl trichloromethylphosphonate by anhydrous potassium fluoride to give diethyl phosphorofluoridate. This, too, appears to be a rather clean reaction but the fate of the potassium and the trichloromethyl group is not known at present. This we also hope to investigate in the future.

A. F. Isbell
Principal Investigator

REACTION OF PHOSPHORUS ESTERS WITH SODIUM IN TOLUENE AT 110°C.

TABLE I

Esters	Results
Dimethyl methylphosphonate	Reacted readily. Gave 1150 ml. gas (methane) from 0.1 mole ester. Also gave white, insoluble solid.
Dimethyl methylphosphonate	In this reaction, solvent was excess ester and no toluene. Only 35 ml. gas produced from 0.1 g. atom Na. Solid product soluble in excess ester.
Diethyl ethylphosphonate	Reacted readily. Gave 1100 ml. gas (ethane) from 0.1 mole ester. Also gave white, gummy solid.
Diethyl ethylphosphonate	In this reaction solvent was excess ester and no toluene. Solid product soluble in ester but slowly separated as large colorless crystals on standing for some days.
Di-n-butyl n-butyl-phosphonate	Reacted readily. Gave 710 ml. gas (butane) from 0.1 mole ester. Solid product gave viscous gel in toluene.
Di-n-butyl benzylphosphonate	Reacted readily. Gave 750 ml. gas (no identified) from 0.1 mole ester. Also gave white, insoluble solid.
Trimethyl phosphite	No reaction.
Triethyl phosphite	No reaction.
Tri-n-butyl phosphate	No reaction.
Triethyl α,α-dimethylphosphonoacetate	Reacted readily. Gave 2.3 l. gas (ethane) from 0.1 mole ester. Also gave white, insoluble solid.

TABLE I (Continued)

Esters	Results
Triethyl phosphonoformate	Reacted rapidly. Gave 2.2 l. gas (not identified) from 0.05 mole ester. Also gave brown, insoluble solid.
Diethyl phenylphosphonate	Reacted readily but only 200 ml. gas (not identified) produced from 0.15 mole ester. Also gave white, insoluble solid.
n-Butyl n-butylethylphosphinate	No reaction.
Ethyl diethylphosphinate	No reaction.